# Trace Element and Nutrient Cycling in San Francisco Bay

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# LONG-TERM GOALS

The long term goal of this research is to examine the processes that control trace metal concentrations in near-shore waters. Within this context, we examine the role of chemical exchange across the sediment-water interface and the examine how changes in harbor processes will affect water column trace metal burdens. This research represents the collaboration between scientists with expertise on biogenic matter degradation (W.B., USC) and trace metal analyses (K. Coale and K. Johnson, Moss Landing Marine Labs) with the long-term goal to develop and integrated understanding of trace metal behavior in near-shore sediments.

# **OBJECTIVES**

One objective of this research is to examine the processes that control trace metal exchange across the sediment-water interface. This involves studying transport mechanisms (diffusion and bio-irrigation) and studying the processes that influence the concentration of dissolved metals within interstitial waters. The role of organic carbon remineralization and the pathways by which terminal electron acceptors are utilized to solubilize trace metals is a major focus of this research. Other objectives of this research are to develop an advanced form of the 'standard' benthic flux chamber for use in near shore environments, test this device, and utilize it for research in San Francisco Bay.

Further, we also set a goal to develop a quantification of benthic macro-faunal activity and its relationship to fluxes of trace metals.

#### **APPROACH**

Our approach has been to measure dissolved trace metals (As, Ni, Fe, Mn, Co, Cu, Cd), nutrients and gases (oxygen, nitrate, ammonia, phosphate, silicate, TCO<sub>2</sub>, alkalinity and radon-222) from pore waters and in incubation chambers collected and deployed in S. San Francisco Bay. Research was coordinated between USC, MLML and USGS scientists so that an optimal amount of measurements could be made during a field session of 8-12 days. The benthic chamber deployments were conducted utilizing a new chamber designed for this project and older chambers for intercomparison purposes. Sediment cores were collected remotely by the new chamber and by divers at various S. Bay sites. The depth distribution of metals and nutrients was determined and modeling has been underway to derive diffusive flux estimates from these data. Trace metal measurements on small volume samples were made by the MLML group using chemiluminescent flow injection techniques. The USC group made the nutrient and gas measurements. Modeling the distribution of an introduced tracer (CsBr) within the chamber and sediment pore waters was used to provide a quantification of transport mechanisms, depths and rates.

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1. REPORT DATE 1998 2. REPORT TYPE				3. DATES COVERED <b>00-00-1998 to 00-00-1998</b>		
4. TITLE AND SUBTITLE				5a. CONTRACT NUMBER		
Trace Element and Nutrient Cycling in San Francisco Bay				5b. GRANT NUMBER		
				5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S)				5d. PROJECT NUMBER		
				5e. TASK NUMBER		
				5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  University of Southern California, Department of Earth Sciences, Los Angeles, CA,90089-0740				8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)		
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAIL Approved for publ	ABILITY STATEMENT ic release; distributi	ion unlimited				
13. SUPPLEMENTARY NO See also ADM0022						
14. ABSTRACT						
15. SUBJECT TERMS						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON	
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE unclassified	Same as Report (SAR)	4		

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Form Approved OMB No. 0704-0188 Studies were completed whereby the benthic biota within the benthic chamber were perturbed in various ways to simulate natural disturbance processes. Manipulation experiments included the addition of acid, oxygen, formaldehyde, molybdate and clams into a chamber. USGS scientists (J. Kuwabara) were involved with the measurement of DOC and sulfide in chambers and pore waters and J. Thompson advised us regarding biological manipulations.

#### WORK COMPLETED

We successfully completed three research cruises in Los Angeles/Long Beach Harbor in 1994-1996 and recently completed three research cruises in S. San Francisco Bay in April and July 1997 and September 1998. Work in April was conducted at 3 sites, in July at 2 sites and in September we focused on 1 site.

The newly developed chamber worked very well. The new chamber has a lid that can open and close, has greater flexibility with spike injections and has a remote coring device. Very high quality data and samples were collected on all three cruises. Samples from chambers and pore waters are archived at both MLML and USC.

Data analysis and modeling have proceeded very well. We have quantified the fluxes of trace metals and nutrients from various sites within the Bay and have many (>10) pore water profiles for metals and nutrients. We have also sampled the water column of the Bay for nutrient and metal loads. During the last field endeavor, we deployed and recovered 6 benthic chambers and collected 7 cores from a site on the western shoals of S. San Francisco Bay.

## **RESULTS**

Results from a comparison of the new and old benthic chambers indicate that both produce the same results, although the new chamber has several key advantageous features. Intercomparisons were completed on all three cruises in San Francisco Bay.

Fluxes of nutrients (ammonia, silicate, TCO<sub>2</sub>) were much higher at a station in the eastern portion of S. San Francisco Bay in April as compared with July, 1997. It is likely that the fluxes we measured reflect the timing of our field work, close to the spring bloom deposition of phytoplankton. By July, most of the deposition pulse was degraded. Dissolved silica fluxes were especially large in April, reflecting the unusually high proportion of diatoms in the spring, 1997 bloom (J. Thompson, pers. comm.). The rate of oxygen consumption in bay sediments is cut by approximately 1/3 following the addition of formalin to a benthic chamber, suggesting that irrigation is responsible for a large fraction of the total flux. The formalin treated chamber showed a siliceous acid flux comparable to the flux in the untreated chambers indicating the abiotic control of silicate dissolution.

Chamber results from the Sept. 1998 deployments are still being worked up. We conducted several experiments whereby a plot of sea floor was incubated under control conditions and the same plot was incubated after the addition of <u>Potamocorbula sp.</u> clams. Preliminary results indicate a measurable effect of clam densities on nutrient regeneration rates.

Another important result of the research was the development of models to describe the behavior of Br tracer within a benthic chamber. A modeling program was designed to fit observed Br vs. incubation time plots and predict bio-irrigation rates. We combine the Br tracer model results with radon-222 flux

data and are able to constrain the irrigation rate (ml/hr) and depth in the sediments to which irrigation occurs.

Irrigation rate has a positive Impact on the efflux of Cd, but a negative impact on the flux of Mn and Co. Results of pore water profile modeling indicates that the diffusive flux is a fraction (< 30%) of the total flux measured by the chambers.

#### **IMPACT/APPLICATIONS**

This research has direct bearing on our understanding of trace metal distributions in near-shore waters. It will show how changes in the ambient environment (eutrophication, invasion of exotic species, changes in the availability of oxidants) may affect the flux and availability of various toxic metals. This work provides measurement constraint for contaminant modeling by defining the residence time of water in contact with the sediment interstitial water. Another impact of this research has been the development of a new style of benthic chamber, one that is better suited for work in near-shore environments and specifically designed for conducting manipulation experiments.

The manipulation experiments with the exotic clam <u>Potamocorbula sp.</u> allow us to separate the impact of invasive species from natural processes.

# **TRANSITIONS**

The new benthic chamber has been used in collaborative research with Australian scientists (D. Heggie, AGSO; W. Dennison, U. Q.) in studies of the benthic chemistry of Moreton Bay, Australia. Our results will be utilized by scientists at the USGS as part of their ongoing studies of San Francisco Bay biogeochemistry. We have plans to present seminars describing our results to the USGS in 1999.

## RELATED PROJECTS

The study in Moreton Bay, Australia benefited from the work accomplished under ONR funding. There, the research focus was on nitrogen cycling in sediments influenced by the outflow of the Brisbane River.

Two proposals (pending) regarding research in Santa Monica Bay will take advantage of things learned during the ONR research and will also utilize the new benthic chamber. I have a collaborative project funded through the USGS to work with survey scientists on a study of trace metal fluxes from Lake Coeur d'Alene, Id. This project is funded by EPA.

## **PUBLICATIONS**

T. H. Townsend (1998). Numerical simulations of tracer loss from benthic chambers: An investigation of bio-irrigation rates and patterns in marine sediments. MS Thesis, University of Southern California, pp. 173.

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